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Patent specifications:	German Patent Application No. 102 34 507.4 (Patent claims / Description / Abstract)
Title:	DE: Verfahren zur örtlich hochaufgelösten massenspektroskopischen Charakterisierung von Oberflächen mittels einer Rastersondentechnik
	EN: Method for locally highly resolved, mass-spectroscopic characerization of surfaces using scanning probe technology
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Method for locally highly resolved, mass-spectroscopic characterization of surfaces using scanning probe technology

The present invention relates to a method for high-resolution microscopic observation of the surface structure, and at the same time of the molecular composition associated with the observed structure elements, of a sample surface. The invention also relates to an apparatus consisting of a specially adapted scanning force microscope and a specially adapted mass spectrometer for carrying out the method according to the invention.

A scanning force microscope (SFM) scans the surface structure of a sample to be examined, by means of a piezoelectric mechanism. The mechanism can be moved not only on the sample plane (x/y direction) but also at right angles thereto (z direction). First of all, the sample is moved into contact with a tip by moving it in the z direction. The tip is located at the free end of a cantilever which is clamped in at one end. The cantilever typically has a length of between 10 µm and 500 µm, and the tip is ideally atomically sharp. The cantilever and tip are generally integrated and, in most commercial products at the moment, are composed of silicon or silicon nitride. The bending of the cantilever as a result of the force between the sample and the tip is normally measured by means of the optical pointer principle, and is set to a desired (nominal) value.

In the so-called contact mode, an image of the sample surface is obtained as follows: while a section of the sample surface is being scanned, any further bending of the cantilever resulting from the sample topology is fed back to the nominal value. The setting of the scanning unit in the z direction as a function of each point on the x/y plane reflects the sample topology, and is recorded.

In the so-called intermittent contact mode, the cantilever is caused to oscillate close to its mechanical resonant frequency before being moved towards the sample. After being moved towards the sample, the tip then touches the sample briefly on one occasion in each oscillation cycle. This leads to attenuation of the oscillation and thus to a reduced oscillation amplitude, which is measured and is set to a specific value as a measure of the intensity of the interaction between the sample and the tip. The sample surface is now imaged as described above.

Time-of-flight (TOF) mass spectroscopy is used to examine the molecular composition of an analyte on the basis of the molecular masses of the components. The elements of a sample to be examined are changed from the solid phase to the gas phase in different ways in a vacuum system. Inter alia, one sample region is bombarded with a laser pulse for this purpose. In the

process, charged molecules or molecule fragments which are accelerated by means of electrodes in a flight tube from which the air has been removed strike a detector after a flight path of approximately 60 to 100 cm. The molecular weight is calculated from the time of flight: the heavier the molecule, the longer is the time of flight. This method is extremely sensitive and accurate; only subpicomolar quantities are required. In principle, it is technically possible to detect individual ions in a TOF arrangement. The error is around ± 0.05 Da per 1000 Da.

The primary aim of scanning force microscopy is to allow the state of a sample surface to be assessed by imaging the structure. If the preconditions are ideal, the atomic structure of a sample surface can be resolved. This applies to surfaces of crystalline structures and, to a restricted extent, to high-order organic and inorganic adsorbates on surfaces. In these situations, the state of the sample surface can be assessed directly.
However, depending on the sample, this resolution is generally not achieved and the topography does not provide sufficient information to make an assessment of the state of a sample surface. In these situations, it is necessary to identify the local chemical nature or the local molecular composition of a sample surface by means other than microscopic structure analysis. This statement moreover relates not only to scanning force microscopy but also to any other microscopic method (electron microscopy, optical microscopy, etc.). Methods are therefore used which combine microscopic imaging with chemical analysis, in the wide or narrow sense. The following text describes the two methods which are related to the method according to the invention and are based on local ablation of the surface, followed by mass spectroscopy.
In laser desorption mass spectrometry (LAMMA), a laser pulse is focused onto a sample point chosen by means of conventional optical microscopy. This leads to local ablation of the sample and to the production of molecule ions from the locally ablated material. The ions are accelerated in the electric field and are identified on the basis of their molecular mass by means of a time-of-flight mass spectrometer. A new LAMMA arrangement (LAMMA 2000; Spengler B. and Hubert, M. (2002)) should be mentioned in particular, in which the described principle has consequently been optimized for combined imaging of the structure by means of confocal optical microscopy and local molecular composition by means of mass spectrometry of samples. In this arrangement, both the optical resolution and the minimum sample region from which ions can be obtained and detected are diffraction-limited. An optical and

analytical resolution of 0.5 µm has been achieved in practice (that is to say the minimum analyzed sample region had a diameter of 0.5 µm).

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is one analytical method for locally resolved chemical characterization of material surfaces of an inorganic, organic and biological nature. The method is based on time-resolved recording of secondary ions which are produced by bombardment of the surface with high-energy primary ions (Cs+, Ga+). In this case, the primary ion beam is highly focused and is scanned over the sample. The secondary ions released during the process are accelerated into the flight tube of a TOF mass spectrometer. Since the effective verification depth is only about 1 nm, the measured mass spectrum is composed only of the chemical components from the uppermost molecular layers. The lateral resolution of the ion images is about 1 µm.

The above methods for locally resolved chemical characterization of a sample surface vary with respect to the minimum analyzed sample region within the resolution range of conventional optical microscopy. This is inadequate for many requirements in medicine, engineering and science. By way of example, cell membranes are laterally organized in a complex manner. In this case, so-called lipid rafts represent the functional units of a large number of membrane-bound processes. Their diameter is about 60 nm. Analysis of their individual composition would be of critical importance for a complete understanding of the membrane-bound processes that have been mentioned.

The combination of structure imaging in the nanometer range with mass spectroscopy with corresponding local resolution promises an answer to the requirements that have been mentioned, and to a large number of other requirements. A combination of a scanning probe technique (for example, SFM) with mass spectroscopy may primarily be used for this purpose. In fact, so far, the option of a combination of mass spectroscopy with high-resolution scanning force microscopy has been investigated in different ways by different authorities. Either sample material has been deliberately ablated by lateral injection of pulsed laser light into the gap between the sample and the SFM tip, or pulsed laser light has been used to illuminate the sample, in the form of a pulse, through a glass fiber with a conical tip in a so-called aperture SNOM (scanning near-field optical microscope). Both strategies make use of the principle of near-field optics, that is to say the tip is used to produce an illumination spot which is considerably smaller than the smallest possible diameter of an illumination spot produced by conventional optics. In fact, this has made it possible to reproducibly produce

holes with a diameter of a few nanometers. In both cases, ions that were produced were sucked out laterally from the tip region. However, it has not so far been reliably possible to achieve an unambiguous association between ions and a defined region in the near field of the tip. This problem is a result of the ions being sucked out inefficiently from the near field of the tip and sample. Our own experimental investigations and model calculations by means of SIMION (citation) have confirmed the unsatisfactory finding: the transmission of ions that are produced into the flight tube of a mass spectrometer is poor and is dependent in a manner which cannot be calculated on the geometric conditions immediately at the point at which the ions are produced.
In summary, universal chemical analysis of surfaces with a local resolution in the nanometer range has not yet been available.

The object of the invention is therefore to specify an improved method and an improved apparatus in which ions are produced in a very small volume in the near field of a tip/sample region which can be selected by the scanning force microscope, and which by means of a special choice of arrangement are also passed on with a high transmission level for mass spectrometry.
In particular, the method allows

- an unambiguous association between all the observed ions and a defined sample region;
- association of the observed ions with the sample topology;
- local resolution, both of the topology and of the local molecular composition, below the resolution limit of conventional optical systems.

According to the invention, the object is achieved by a method in which a scanning force microscope is operated with a cantilever with an integrated hollow tip. The hollow tip has a small aperture opening on the sample side. The aperture preferably has a diameter which is considerably smaller than the wavelength of the light that is used. An illumination spot is thus produced on the sample on the basis of the principle of near-field optics, with a diameter which is considerably less than the diffraction-limited illumination spot of conventional optics. The cavity of the tip widens increasingly towards the rear side, where it has its largest opening.

Scanning force microscopy is preferably carried out conventionally, as described above, in the intermittent contact mode or the contact mode. The microscopy is preferably carried out in a high vacuum. As an alternative to scanning force microscopy, it is also feasible to adapt other scanning probe techniques for use in the described method.
The locally resolved mass spectroscopy is carried out in parallel with or following the SFM imaging. In this case, the tip is in contact with the sample, or is in the immediate near field of the sample. For mass spectroscopy, a laser pulse is injected axially into the hollow tip from the rear side. Material is ablated from the sample at each desired point on the sample by means of a short laser pulse, and is passed on for mass spectroscopy. For this purpose, the opening in the rear of the tip is axially adjoined by a flight tube, which is at a suitable electrical potential relative to the tip and to the sample and is used for electrically sucking out the molecular ions which are produced after a laser pulse. The ions then preferably fly into a time-of-flight mass spectrometer.

Further advantages and expedient developments of the invention will become evident from the following description of exemplary embodiments and with reference to a drawing, in which:

Figure 1 shows the basic structure of the method according to the invention, a cross section through the scanning unit, the sample, the cantilever with a hollow tip, the flight tube and the objective; variant 1

Figure 2 shows the basic structure of the method according to the invention, a cross section through the scanning unit, the sample, the cantilever with a hollow tip, the flight tube and the objective; variant 2

Figures 1 and 2 show two variants of the basic structure of the method according to the invention. In both cases, scanning force microscopy is combined with the capability to ablate surface material from the sample at any point x, y, and to carry out mass-spectroscopic analysis of ionized sample material. This is done by using a cantilever 1 with a tip 2 having a continuous, axial, conical cavity. The cavity opens with a defined aperture at the apex 3 of the tip.

The aperture serves as an outlet opening for a focused laser pulse 10 onto the sample 30, and as an inlet opening for molecular ions 20 which are produced after a laser pulse in the area of the illuminated sample region.

The sample is generally illuminated coaxially with respect to the longitudinal axis of the tip, through the cavity therein. The ions are preferably likewise extracted coaxially with respect to the tip and through the cavity. For extraction, the flight tube 21 is placed at an electrical potential relative to the sample. An electric field is formed, largely axially symmetrically with respect to the flight tube/tip axis. The field penetrates the cavity of the tip and leads to extraction of the ions. If the flight tube is at a relative negative potential, ions with a positive total charge are extracted, and vice versa. The high degree of axial symmetry of the arrangement and thus of the field leads to a largely axial extraction and to an axial flight of the ions. Additional ion optics in the flight tube (not illustrated) serve to pass back ions which do not fly exactly axially.

The area from which the material is ablated is defined by the size of the aperture in the hollow tip. The aperture diameter is typically considerably less than the wavelength of the light that is used.

Variants 1 and 2 differ in how the laser light is injected: in variant 1, an objective 11 is located at the side, alongside the flight tube, for focusing. The optical axis 12 is initially at right angles to the axis of the flight tube 21. The light enters the flight tube via a window, is deflected in the axial direction by means of a mirror 13, and is focused into the cavity of the tip. The mirror has a central hole 24 for the ions to pass through.

In variant 2, the objective is coaxial with respect to the flight tube. The flight tube is introduced into a central hole 24 in the objective. Collimated laser light is reflected into the beam path behind the objective. In this case as well, the mirror has a central hole for the ions to pass through.

Claims

1. An apparatus for a scanning probe microscope, in particular a scanning force microscope, equipped with a measurement probe which defines a near field, and a scanning unit which allows the measurement probe to move relative to a sample in all three spatial directions, in conjunction with a mass spectrometer with an ionization unit formed in particular by a laser, an extraction unit formed in particular by an electric field, and an analysis unit formed in particular by a time-of-flight secondary ion mass spectrometer, characterized in that the ionization unit uses the near field of the measurement probe in such a way that ions are formed only in the near field of the measurement probe, and the shape of the measurement probe allows a largely undisturbed axially symmetrical field distribution of the extraction unit with respect to the axis of the analysis unit, in particular the flight tube.

2. The apparatus as claimed in claim 1, characterized in that the measurement probe is a cantilever with a hollow tip.

3. The apparatus as claimed in claim 1 and 2, characterized in that all presently known methods, in particular the optical pointer principle and the piezoresistive method, can be used to detect the bending of the cantilever.

4. The apparatus as claimed in claim 1, characterized in that the scanning unit moves the sample in all three spatial directions.

5. The apparatus as claimed in claim 1, characterized in that the ionization unit is a laser which is focused non-axially preferably onto the sample, preferably by means of high-number optics, such as e.g. an objective, and then is deflected into the axial direction by means of a mirror, with the mirror having to have an axial hole which allows the ions to pass through to the analysis unit.

6. The apparatus as claimed in claim 1, characterized in that the ionization unit is a laser which is deflected into an axial direction by means of a mirror, and then is focused preferably onto the sample by means of high-number optics, such as e.g. an objective,

with the mirror and the focusing device each having to have an axial hole which allows the ions to pass through to the analysis unit.

7. The apparatus as claimed in claim 1, characterized in that the ionization unit is a laser which is deflected non-axially onto the probe, and ionization in the near field of the probe is caused, e.g., by means of field amplification.

8. A method for high-resolution examination of a measurement sample using a combined scanning probe microscope, in particular a scanning force microscope, characterized in that the scanning probe microscope is first of all used to record an image of the sample, in particular of the topography, and then a destructive chemical characterization of selected areas of the sample takes place using a mass spectrometer.

9. The method as claimed in claim 8, characterized in that the selected areas are chosen successively such that the entire area imaged by the scanning probe microscope is analyzed, thus additionally resulting in a chemical image of the sample.

10. The method as claimed in any one of claims 8 or 9, characterized in that further ablation leads to high-resolution depth information.

11. The method as claimed in any one of claims 8 to 10, characterized in that the distance between two points for ionization can be chosen by analysis of the area ablated by an ionization process, such that this leads to uniform ablation of the sample.

12. The method as claimed in any one of claims 8 to 11, characterized in that the information from scanning probe microscopy and from mass spectrometry can be compared with high lateral resolution.

Abstract

The method according to the invention combines the highly resolved imaging of a sample surface by means of scanning force microscopy and the correlated locally highly resolved chemical or molecular nature of the sample surface by means of mass spectroscopy. The chemical analysis of the surface takes place after laser desorption of a restricted surface region. To this end, the surface is illuminated by pulses at any point of interest in accordance with the optical near-field principle. The optical near-field principle guarantees an analysis with a non-diffraction-limited local resolution. The hollow tip allows unambiguous association of the chemical analysis with a selected surface region. The highly symmetrical arrangement allows a high transmission of the molecular ions produced.

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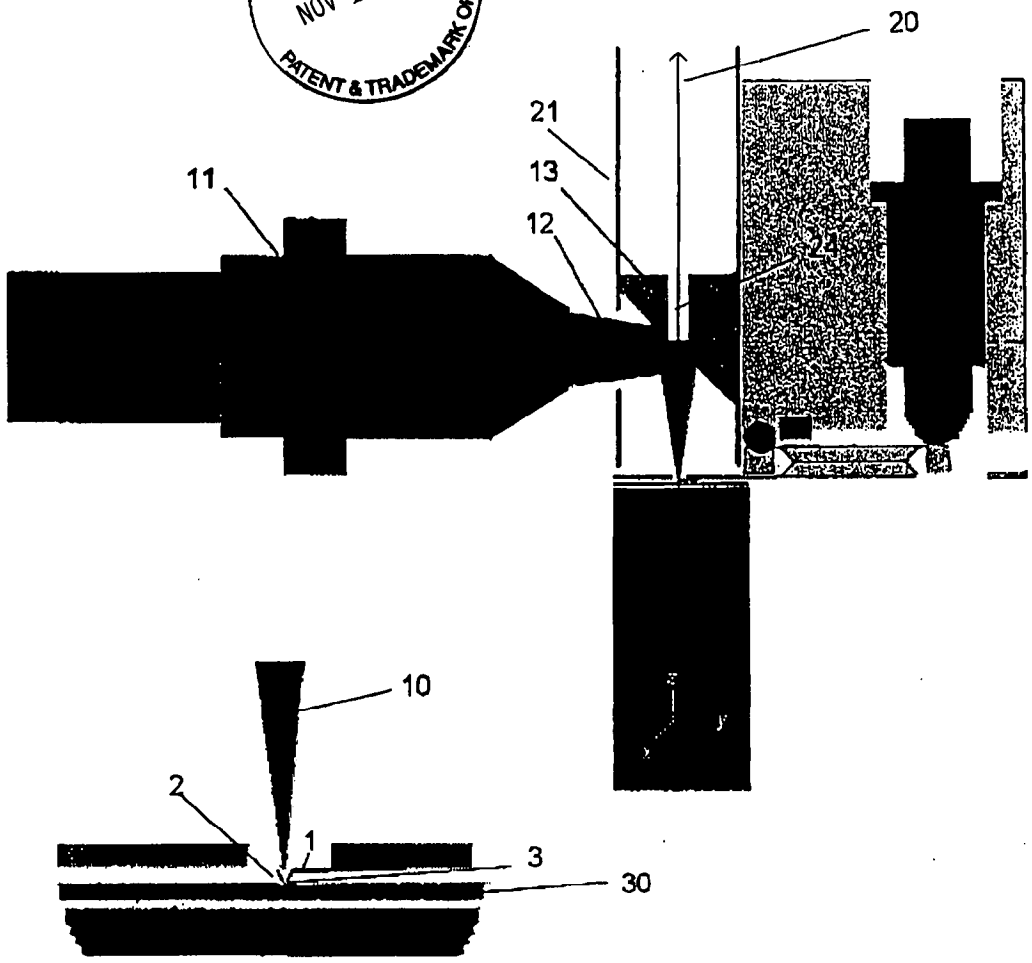

Fig.1

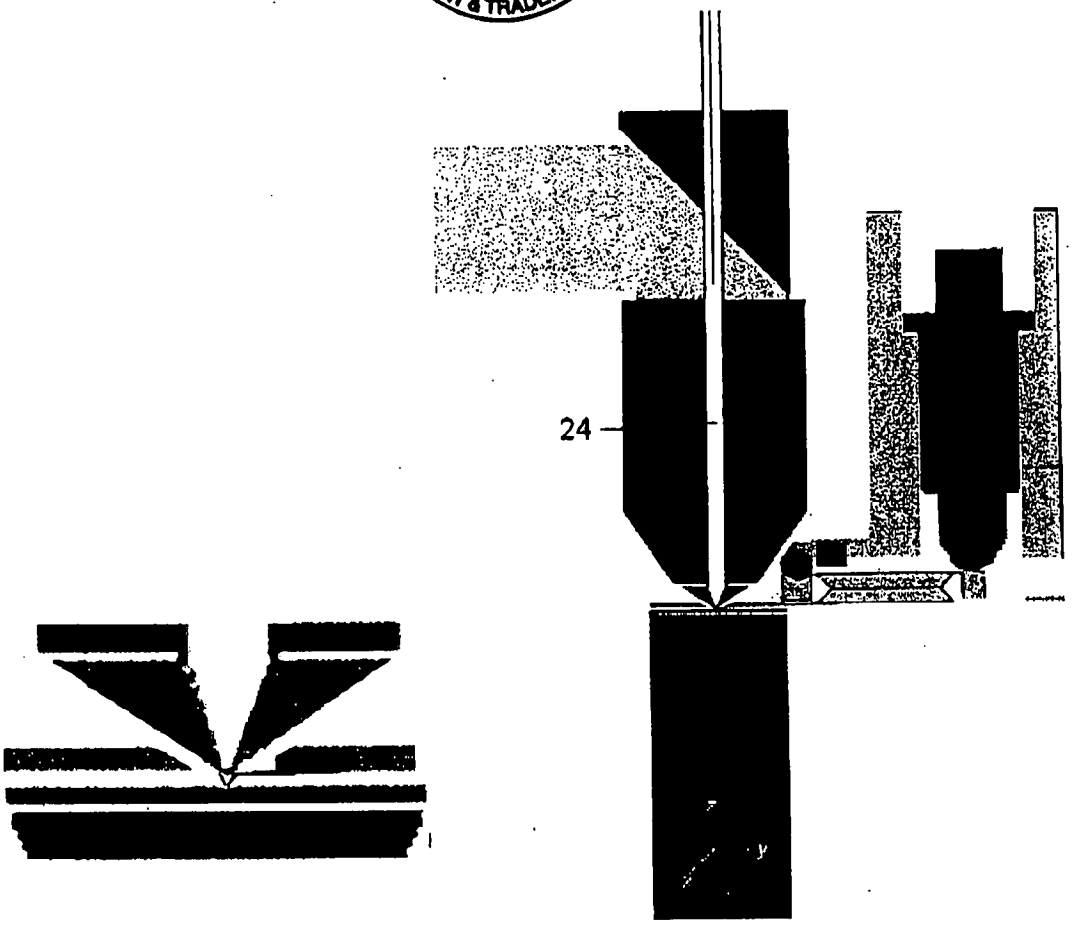

Fig.2